

CO₂ utilization in the perspective of industrial ecology, an overview



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ABSTRACT

Carbon dioxide emissions from anthropic activities have accumulated in the atmosphere in excess of 800 Gigatons since preindustrial times, and are continuously increasing. Among other strategies, CO₂ capture and storage is one option to mitigate the emissions from large point sources. In addition, carbon dioxide extraction from ambient air is assessed to reduce the atmospheric concentration of CO₂. Both direct and indirect (through photosynthesis) pathways are possible.

Geological sequestration has significant disadvantages (high cost, low public acceptance, long term uncertainty) whereas carbon dioxide recycling (or utilization) is more consistent with the basic principle of industrial ecology, almost closing material cycles.

In this article, a series of technologies for CO₂ capture and valorization is described as integrated and optimized pathways. This integration increases the environmental and economic benefits of each technology. Depending on the source of carbon dioxide, appropriate capture and valorization processes are evaluated based on material and energy constraints.

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1. Introduction

Almost closing material cycles is a fundamental principle of industrial ecology. Carbon dioxide utilization (CCU) is obviously more consistent with this principle than carbon capture and sequestration (CCS). Besides, it adds value to the captured carbon and can partially substitute for fossil reserves [1]. In addition, CCU avoids the problems of costs and public acceptance which hinder CCS. If capture of CO₂ from concentrated industrial sources is largely assessed to minimize new emissions, the extraction of atmospheric CO₂ is also needed to address diffuse sources and tightly close the anthropogenic carbon cycle. Two options are possible, direct air capture (DAC) [2] and bioenergy with carbon capture and storage (BECCS) [3].

Chemical utilization of CO₂ is a challenge given the stability of the molecule. Usually, energy-rich co-reactants such as hydrogen are needed. The primary energy used for the production of these molecules should be renewable in order to ensure the sustainability of the whole process. In addition, availability of certain critical resources, particularly water and metals, must be accounted for. Therefore, CCU must be assessed in detail and considered as part of an integrated process, from the CO₂ capture to the final transformation. The variety of products that can be synthesized from CO₂ is particularly promising given the range of conceivable strategies, as described by several reviews [4]. This article consists

of a short description of relevant technological pathways (in the perspective of industrial ecology) for CO₂ capture and utilization (Fig. 1). The benefits of the processes integration are identified.

2. Description of the technologies—capture

2.1. Capture at large point sources

Capture at large point sources is defined as the extraction of carbon dioxide from the flue gases of industrial sources (e.g. power plants, cement or steel factories). Only two technologies are considered in this article: post- and oxy-fuel combustion. In post-combustion, the carbon dioxide is absorbed in a liquid which is then heated at approximately 100 °C to recover carbon dioxide and regenerate the solvent [5]. Two aqueous solutions are commonly used: monoethanolamine (MEA) and ammonia. In terms of industrial ecology, the post-combustion technique is an “end of pipe” solution, having no flexibility and few options for optimization through synergies with other processes. Oxy-fuel combustion (or denitrogenation) consists in combusting the fuel in pure oxygen, releasing a very concentrated stream of CO₂ and H₂O, the latter being removed by condensation. An air separation unit (ASU) usually provides the oxygen on site.

2.2. Direct air capture (DAC)

Outside of academic research, only a few start-ups are testing the concept of DAC. Because of the low atmospheric concentration

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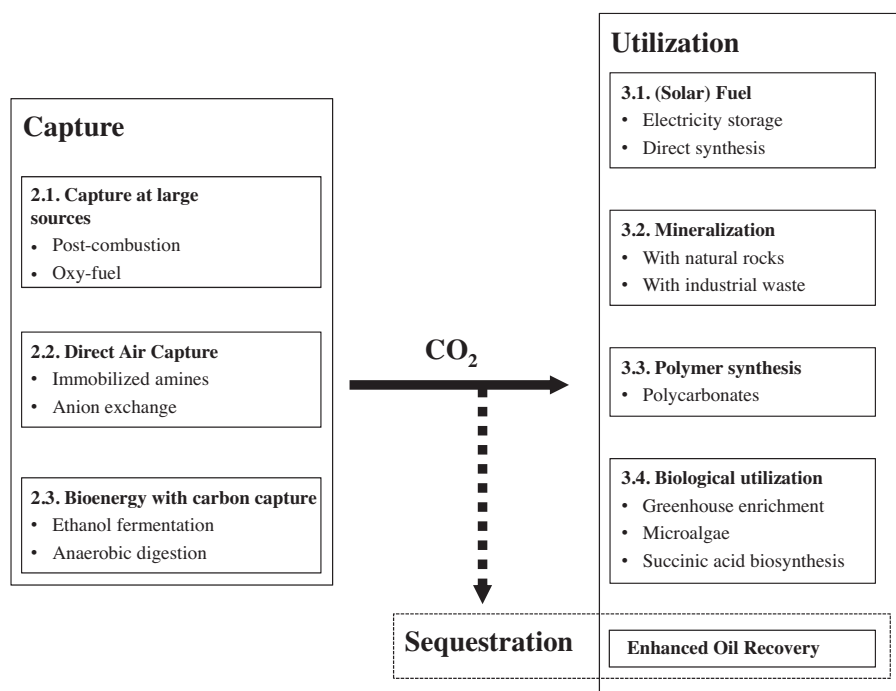


Fig. 1. The processes analyzed in this article.

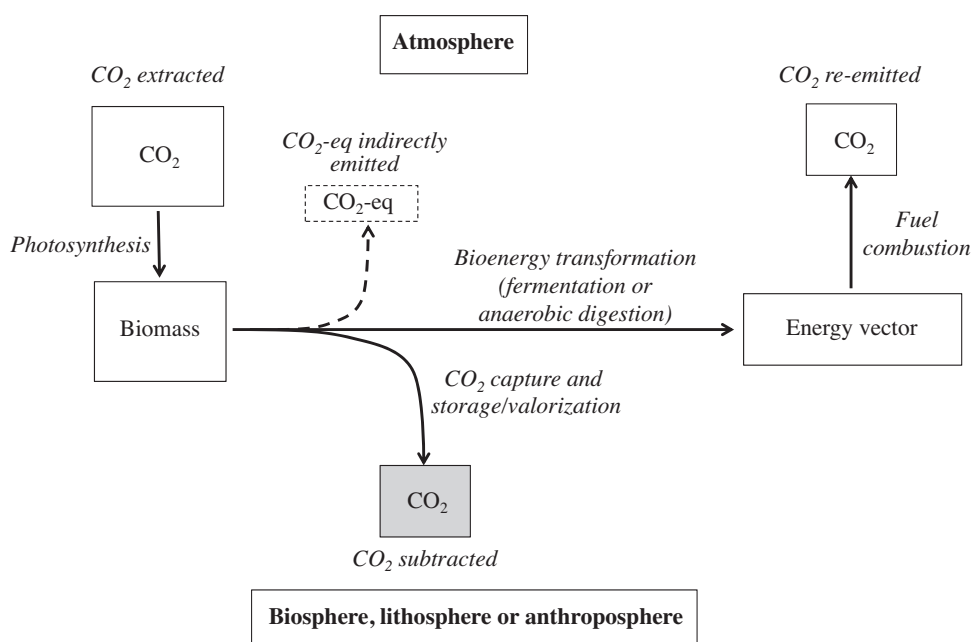


Fig. 2. Bioenergy with carbon capture and storage (or utilization).

(0.04%), DAC requires more energy than capturing CO₂ in flue gases and the processing of considerable volumes of air, typically 2600 mol of air¹ per mole of CO₂ captured [6]. To ensure the sustainability of the process, the energy consumed should be renewable or should rely on heat otherwise wasted (fatal heat). Consequently, two DAC processes accommodating “low temperature” sources (e.g. industrial waste heat or solar power) are considered in this article, adsorption with immobilized amines [7] and with anion exchange resin [8].

2.3. Bioenergy with carbon capture

Capturing the CO₂ emitted by bioenergy production can reduce atmospheric concentration of CO₂ as described in Fig. 2. The general process is called bioenergy with carbon capture and sequestration (BECCS) [3]. The CO₂ can also be reused for chemical, biological or physical purposes (bioenergy with carbon capture and utilization, BECCU).

This article only considers two specific BECCU processes: (1) The capture of CO₂ produced during ethanol fermentation, very concentrated and cheap [9]. (2) The utilization of CO₂ resulting from biogas upgrading.

¹ Calculated with an atmospheric CO₂ concentration = 385 ppm.

3. Description of the technologies—utilization

Currently, the geological sequestration of carbon dioxide is economically viable only if CO₂ is used for enhanced oil recovery (EOR), at the boundary between sequestration and utilization (Fig. 1). Otherwise, approximately 0.2 Gt of CO₂ are used annually by industrial activities, a small amount compared to anthropogenic emissions (32 Gt/yr) [10]. However, new processes are being developed, which should increase this proportion. This section describes the more promising advances in the perspective of industrial ecology.

3.1. Fuel synthesis (solar fuel)

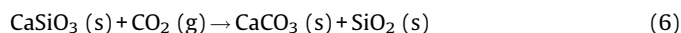
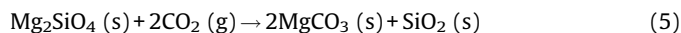
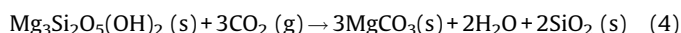
The so-called “solar fuel” concept consists of producing a chemical energy carrier by conversion of solar (or other renewables) to chemical energy. Indeed, the high energetic density of chemical fuels makes them particularly suitable for storing and transporting energy [4c]. Initially, hydrogen produced by water electrolysis was targeted as the energy carrier. However, hydrogen is much more difficult to handle than traditional fuels [11]. The utilization of CO₂ can provide a more convenient (non-fossil) carbon-based solar fuel, without drastic changes to current infrastructures. The process is based on catalytic hydrogenation of CO₂ and can provide, among other products, methane (1), methanol (2) or formic acid (3):



Using solar energy directly, as in photochemical processes, might become another viable option in the mid term [12], but this approach is not considered in this article. Instead, thermochemical strategies are evaluated here since they allow the utilization of a broader range of the solar spectrum. The principle consists of splitting CO₂ in carbon monoxide (CO) and oxygen (O₂). Similarly, water can be split into a mixture of hydrogen (H₂) and oxygen. Carbon monoxide and hydrogen can be further processed in a wide range of fuels by the Fischer-Tropsch process. The use of metal oxides in a looping process is particularly interesting in the first step, producing separately CO and O₂ (or H₂ and O₂). In addition, the decreased reaction temperature (~1500 K, instead of 2500 K for direct splitting) is compatible with solar concentrator technology [13]. Zinc-, ferrite- and ceria-based materials have been tested, and recently reviewed [13–14]. These relatively abundant elements can be employed advantageously for large-scale applications, but it is now necessary to scale up the process in order to evaluate the actual potential.

3.2. Mineralization (production of carbonates)

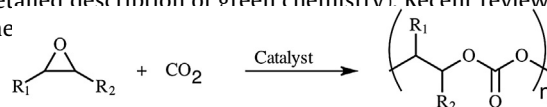
Since the first recognition of the potential of mineralization as a CCS route [15], extensive research has been made to accelerate the reaction, thermodynamically favorable but not kinetically interesting. One strategy consists in activating abundant natural rocks, namely serpentine (Mg₃Si₂O₅(OH)₄), olivine (Mg₂SiO₄) or wollastonite (CaSiO₃) [16]. The carbonation process can be described by the following simplified reactions:



Several routes have been proposed and reviewed in detail. The most promising ones integrate the capture and the mineralization in one step or in a closed loop [17]. Another interesting strategy consists of using brines and alkaline waste materials such as combustion ashes, bauxite red muds or steelmaking slags. The resulting alkaline mixture acts as CO₂ absorbent, producing valuable carbonates such as magnesite [16].

3.3. Synthesis of polycarbonates

The worldwide production of polycarbonates is about 4 Mt/yr and the conventional synthetic route utilizes phosgene [18]. Replacing phosgene with carbon dioxide is more consistent with the principles of green chemistry [19] (see for instance [20] for a detailed description of green chemistry). Recent reviews describe the



Aziridines can also form polymers by reacting with CO₂ under supercritical conditions, producing poly(urethane-amines) [22].

3.4. Biological utilization

Carbon dioxide can be used to enrich the atmosphere of a greenhouse, for boosting plant growth. Several studies have also shown that some microalgae can directly fix carbon dioxide from the flue gases of power plants (the presence of nitrous and sulfur oxides at concentrations up to 150 ppm does not appear to be an inhibiting factor for certain species) [4c,23]. Some cyanobacteria accommodate also wastewater, reducing the fresh water and nutrient consumption and lowering the operational cost [24]. Finally, a few biochemical processes such as succinic acid production incorporate carbon dioxide [25].

4. Integration and analysis of selected CCU pathways

Considering carbon dioxide as a resource rather than a waste implies taking into account different parameters such as purity, reactivity, operational conditions, customer preferences, transportation costs and availability. They influence the transformation chain of CO₂ valorization.

DAC is appealing because the technology can be located almost anywhere, thanks to the rapid mixing of CO₂ in atmosphere. Compared to CCS, the energy consumption and the economic cost are in disfavor of DAC. The costs are estimated at roughly \$27–136/tCO₂ by promoters of air capture, whereas others advance costs as high as \$1000/tCO₂ [26]. In comparison, typical costs of capture at large point sources are estimated in the range of \$20–100/tCO₂ [27], while an ethanol facility can provide high purity CO₂ for \$6–12/tCO₂ [9].

It is very difficult to estimate the purity of CO₂ obtained from different sources. For many catalysts and micro-organisms, traces of acid gases in CO₂ feedstock are problematic. An estimate of the ratio of sulfur dioxide (SO₂) over CO₂ helps predict the purity of carbon dioxide. This ratio is approximately 100 times lower in the atmosphere than in flue gases. Hence, the CO₂ feedstock obtained from direct air capture appears more convenient for further utilization [1,28]. Finally, the carbon dioxide emitted by biological processes is generally very pure and well suited for utilization. For instance, CO₂ emitted by fermentation has a low cost of capture

and purification [4c,9]. The same holds for the CO₂ separated during biogas upgrading, even if its purity is more difficult to predict, depending on the biomass entering the bioreactor and the technical process chosen for purification [29]. In the following sections, different pathways are proposed and analyzed.

4.1. Sequestration, enhanced oil recovery and mineralization

Capturing CO₂ at large point sources reduces emissions from fossil-derived energy. The geological sequestration of CO₂ will probably be needed to a certain extent (Fig. 3, left), considering the amounts of carbon dioxide emitted annually and already accumulated in the atmosphere [30]. Also, the low purity of CO₂ can be detrimental for certain processes of valorization. Capture with aqueous ammonia is very interesting, since regeneration is usually less energy intensive than other processes. In addition, sulfur and nitrous oxide in flue gases are transformed in ammonium sulfate and nitrate after scrubbing. These salts can be used as fertilizers [31].

Enhanced Oil Recovery (EOR) currently uses large quantities of CO₂ captured at concentrated sources. CO₂ is injected into fossil reservoirs to increase the internal pressure and extract more oil. However, uncertainty related to the long-term underground behavior of CO₂ is a concern for both pure geological sequestration and EOR. This uncertainty raises problems of public acceptance and requires costly monitoring of storage sites. Therefore, mineralization is generally considered as a method to store CO₂ more durably and safely (Fig. 3, right). When integrated in the capture step, the process is particularly relevant if silicates rocks are abundant in the vicinity of the CO₂ sources. Carbonates produced have low added value, but can serve as building materials or soil amendments, two applications with large potential (i.e. large quantities of CO₂ used). Finally, the use of industrial alkaline wastes as starting material is possible. It provides an additional service (pollution remediation), but is limited by the amount of industrial alkaline wastes, for instance less than 100 Mt/yr of steelmaking slags [17].

4.2. Microalgae

Microalgae are generally considered as a significant future source of biomass. They can metabolize atmospheric as well as flue gas carbon dioxide. Carbonates are also a convenient source of carbon for certain species. In theory, the culture of microalgae does not require agricultural land and does not compete with food production. However, microalgae are not economically competitive for biofuel production yet.

It has been reported that microalgae can accommodate wastewater, as described in Fig. 4 [24]. This pathway potentially reduces the consumption of fresh water and fertilizers and provides two environmental services (carbon fixation and wastewater treatment). This synergy greatly enhances the competitiveness of the processes and can contribute to the development of microalgae culture. In order to become economically more viable, the microalgae pathway should also be considered within the framework of an integrated biorefinery (see Section 4.4) [12].

4.3. DAC and thermochemical reduction

Given solar irradiance, remote areas (i.e. deserts) represent a large potential for energy collection. However, one issue is transportation of energy from production sites to urban or industrial areas. The synthesis of solar fuels from carbon dioxide is a convenient solution, and direct air capture is likely the most accessible source of carbon dioxide in remote areas. Similarly to air separation units, DAC can be considered as a form of “atmospheric mining”, providing the CO₂ feedstock on site. Various options are possible, such as the association between solar chimney power plants and DAC units in deserts [32] or co-location of wind turbines and DAC units on islands [33].

As described in Fig. 5, solar energy can drive both the capture and utilization steps. The thermochemical reduction (with metal oxide looping) of CO₂ to CO faces apparently no severe material constraints, thanks to the use of abundant metal oxides, but

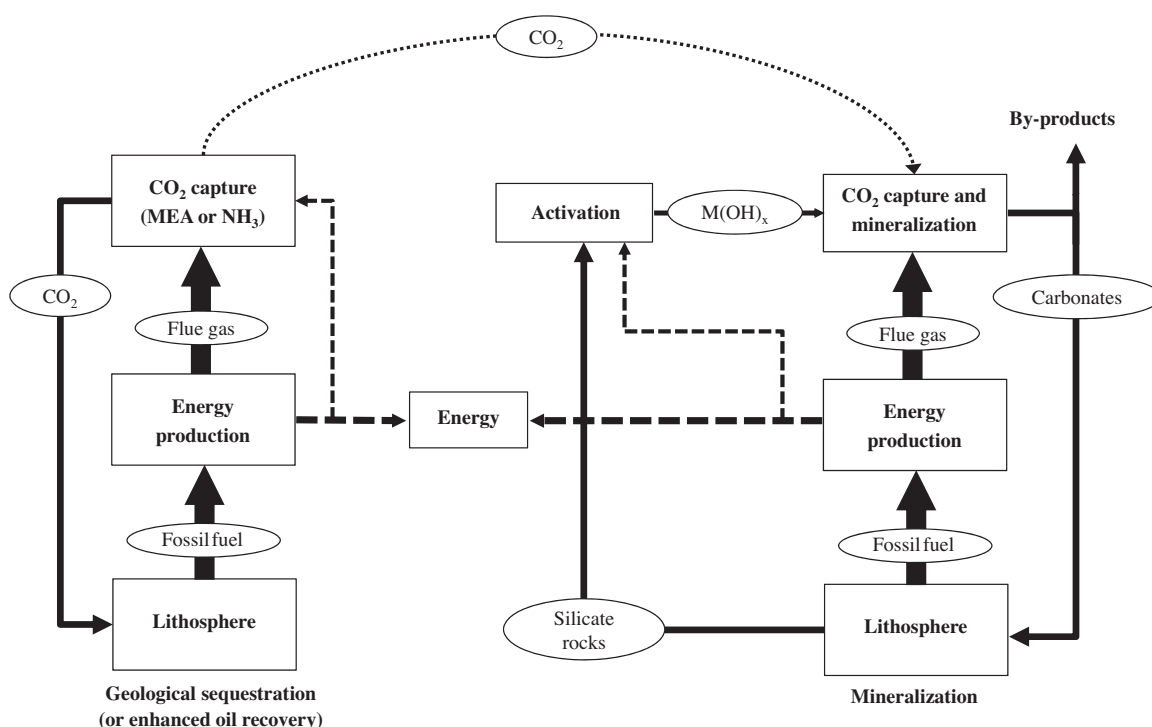


Fig. 3. Geological sequestration, EOR and mineralization.

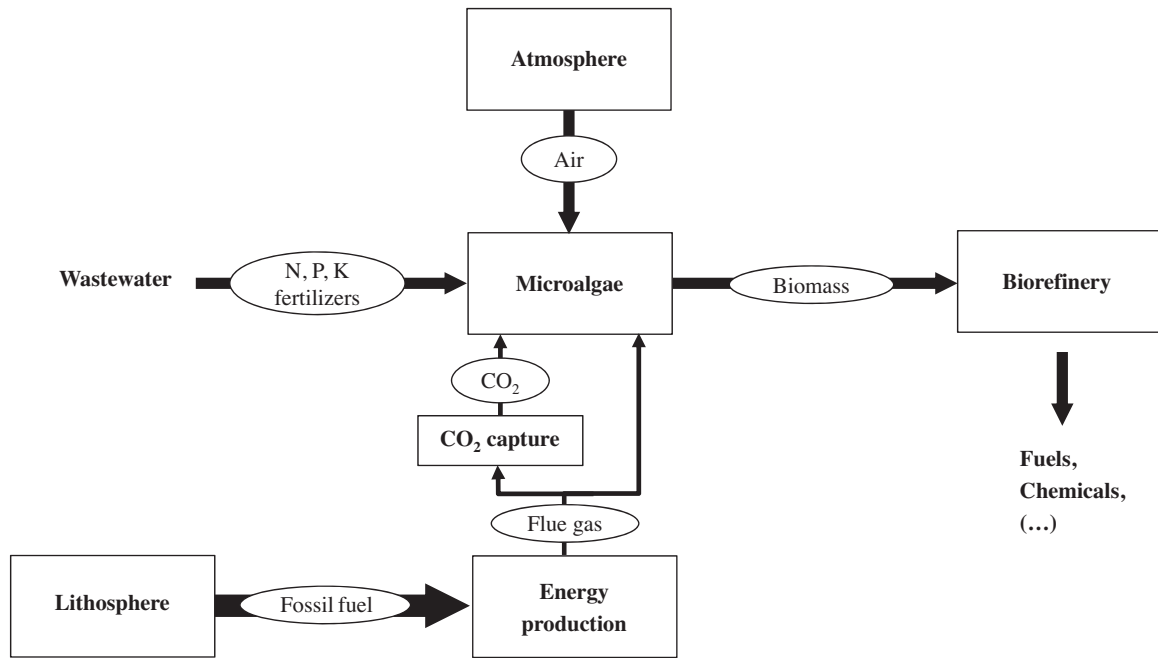


Fig. 4. Microalgae: carbon capture and wastewater treatment.

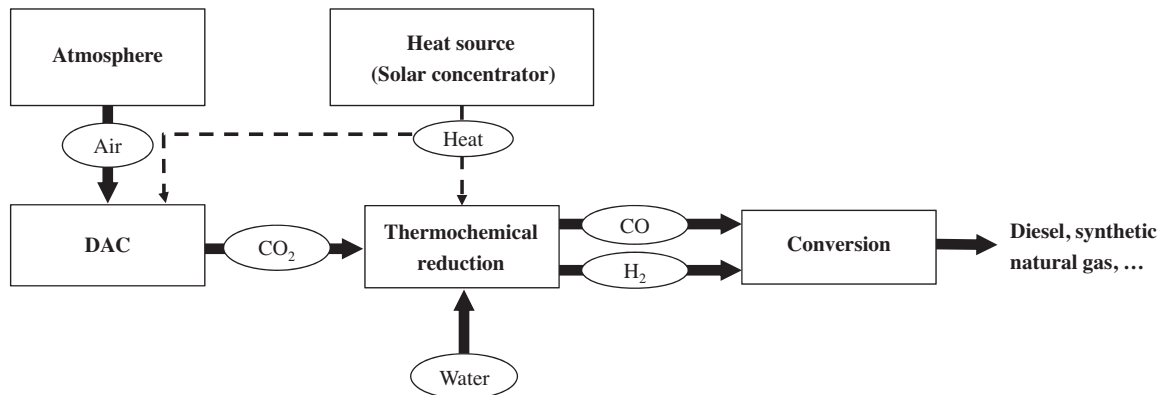


Fig. 5. DAC and thermochemical reduction.

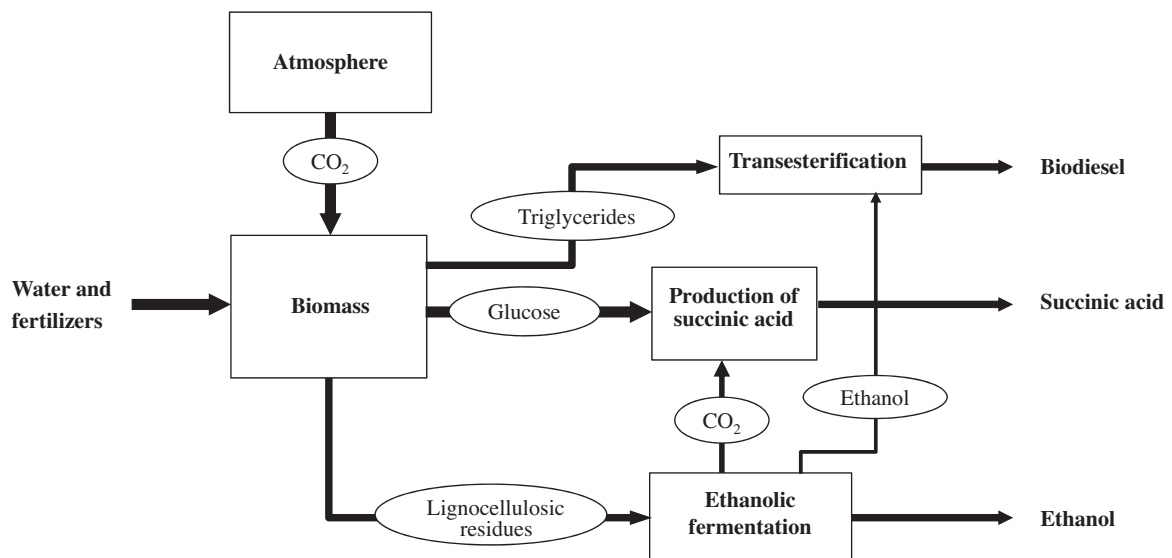


Fig. 6. Integrated biorefinery.

technical challenges remain to be solved, for instance the improvement of solar reactors [14]. Moreover, the bottleneck of this pathway is probably the water required for producing the hydrogen needed to convert CO into fuel in the second step (Fischer–Tropsch process). Water is often a limiting factor in CCU pathways and is obviously scarce in dry areas. It has to be mentioned that immobilized amines adsorb atmospheric water (in addition to CO₂), which could serve as co-reactant, although captured at a high energetic cost [7].

4.4. Integrated biorefinery

Ethanol fermentation releases CO₂ while the biological production of succinic acid absorbs it. Both processes can be coupled to lower overall emissions, as demonstrated by the biorefinery site at Pomacle–Bazancourt in France [25]. Fig. 6 shows the indirect capture of carbon dioxide with biomass (photosynthesis) and the production of ethanol from lignocellulose. The CO₂ released during fermentation is fed into the production of succinic acid. Transesterification transforms triglycerides into biodiesel, using an alcohol. Yet another example of biorefinery configuration would integrate biodiesel from energy crops (or microalgae) and bioethanol production from residues. The limiting factors are essentially related to the availability of biomass, potential competition with food crops, water consumption and fertilizer use.

4.5. Synthesis of carbon negative polymers

Polycarbonate production by co-polymerization typically requires carbon dioxide of high purity, such as the one released by ethanol fermentation. If bio-based compounds replace the fossil-derived epoxides used as co-reactant, the synthesis of polycarbonates becomes highly relevant in terms of green chemistry. Polycarbonates have a relatively long lifetime and their production has reached a large scale. Since epoxides are largely synthesized from olefins, research focuses on substituting fossil-based olefins with bio-based ones [34]. Replacing hydrogen peroxide by dioxygen in the epoxidation of olefins is another route to be explored [4c]. Because biomass already provides various precursors for polymers production, the synthesis of polycarbonates from CO₂ could well be integrated in a biorefinery. Fig. 7 illustrates both options of synthesizing polycarbonates from atmospheric and fermentation CO₂ as well as the development potential in the context of a biorefinery.

4.6. Hydrogenation

If water electrolysis is powered by renewable electricity, the hydrogenation of CO₂ can be thought of as daily or seasonal storage for electrical energy in the form of chemical energy carriers. The products of hydrogenation can be methane (Sabatier reaction), methanol or formic acid. Methane is not toxic, has a cleaner combustion and can be transported over the extensive natural gas network. Methanol is liquid at ambient temperature and atmospheric pressure, which facilitates storage [35]. Methanol is also a starting material in the synthesis of a large number of chemicals, such as formaldehyde and dimethylether. Finally, formic acid could be considered as a way to store hydrogen in liquid form [36], and current research is oriented towards the development of practical H₂ storage-discharge devices [37]. In the perspective of industrial ecology, the production of methane (methanation) is more appropriate thanks to synergies with existing infrastructures, allowing for savings of materials. In addition, methanation is a relatively simple and fast reaction, which can generate methane under atmospheric pressure [38].

Atmospheric as well as CO₂ from biogas upgrading are well suited for methanation. As shown in Fig. 8, multiple synergies exist in the production of fuels, so does the production of methane by methanisation (anaerobic digestion) and methanation (Sabatier). The same infrastructure (e.g. for compression) supports bio-methane and synthetic methane for transport and distribution. Carbon dioxide from biogas upgrading can be fed into the methanation process. Solid and liquid residues from anaerobic digestion can be used as fertilizers, reusing other elements such as nitrogen and phosphorous. Finally, methanation is exothermic and the produced heat can be reused elsewhere, for instance in the CO₂ capture process.

Oxyfuel combustion integrates well with methanation as illustrated on the right side of Fig. 8. Instead of being provided at a high energetic cost by air separation units, oxygen can be sourced as the byproduct of electrolysis [35b,39]. In turn, CO₂ from oxyfuel combustion can feed the methanation process. Ideally, bio- and synthetic methane would completely substitute for natural gas. Limitations in the production of synthetic methane are of two kinds: fugitive emissions resulting from mishandling methane and possibly the availability of water and scarce metals as catalysts. Therefore, nickel based catalysts are probably the most suitable for large-scale implementation of methanation [38].

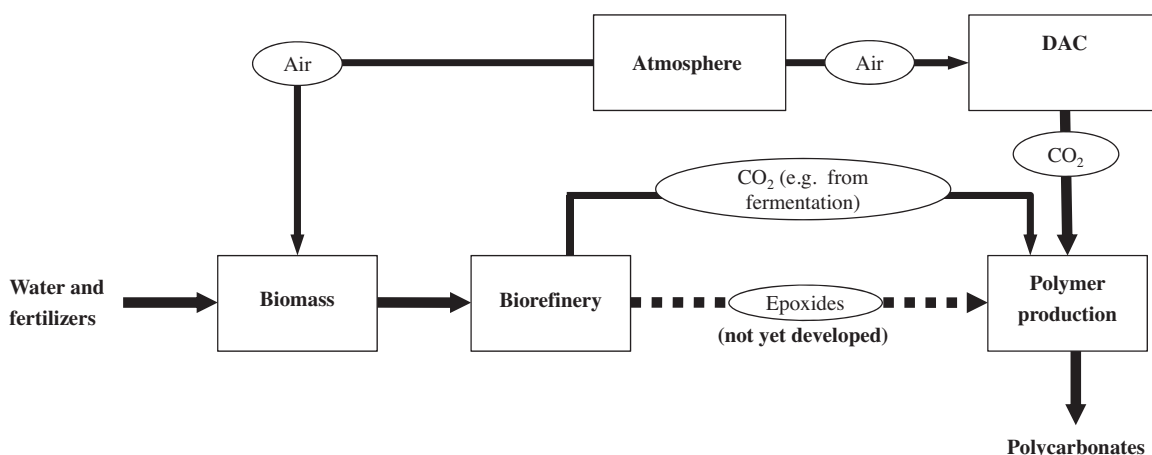


Fig. 7. Biorefinery for polycarbonates production.

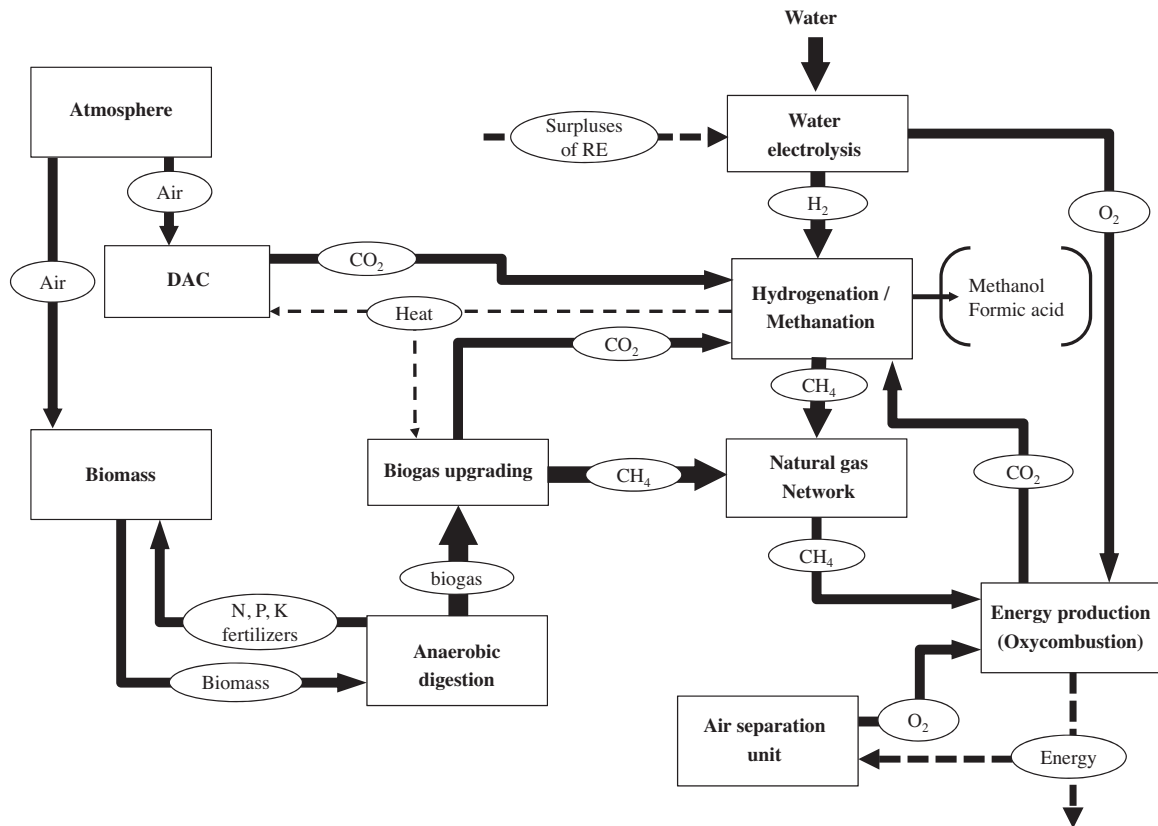


Fig. 8. Hydrogenation.

5. Limitations and research outlook

One of the main principles of industrial ecology consists in promoting (quasi) circular material flows within the economic system. In this perspective, carbon dioxide being a relatively safe, inexpensive and abundant source of carbon, it can be seen as a valuable feedstock. However, strategies for carbon dioxide utilization (or valorization) must be assessed comprehensively, given their potentially far-reaching consequences if implemented on an industrial scale. Using CO₂ as feedstock does not automatically guarantee sustainable or environmentally friendly processes [19]. The main limitations of CCU pathways can be summarized as follows:

- Water consumption, mainly for hydrogen generation and irrigation when biomass is involved
- Requirements of scarce metals, especially for catalysts, but also for infrastructure (e.g. pipelines, renewable energy systems)
- Fossil resource consumption, for co-reactive synthesis (e.g. epoxides, amines)
- Energy consumption, since almost all CCU pathways require energy (even if this can be considered as an advantage for energy storage)

As explained in this article, the design of CCU pathways in an integrated manner reduces such limitations to some extent. By-products exchange and infrastructure mutualization between different industrial processes can help decrease the overall consumption of both materials and energy. When the generation of a waste or a by-product is unavoidable (e.g. oxygen during water electrolysis), its utilization should be foreseen before

implementation. In this perspective, pathways integrating capture and utilization are interesting. For instance, one-pot CO₂ capture, activation and valorization is currently being assessed [40]. In addition, research in the field of biotechnologies, nanotechnologies, photochemistry, catalysis studies or polymer science should be strongly encouraged in order to develop new CCU configurations or optimize existing ones. Carbon dioxide sourced products already have the potential to enter into current economic markets [41]. Moreover, new applications will probably emerge, enabling the use of larger quantities of such products in the economy. Typically, 3D printing could become a large consumer of bio- and/or CO₂-sourced polymers.

6. Conclusion

Current strategies to reduce CO₂ emissions are necessary, but probably insufficient. Once fossil carbon has been extracted and released in the atmosphere, it could be stored in controlled compartments (usually underground) or incorporated in the economic system. On one hand geological CO₂ sequestration faces growing problems of cost and public acceptance. On the other hand, CO₂ can be considered as a raw material and carbon utilization could become the basis for a new anthropic carbon cycle, embedded in the existing natural biological and geological ones. This new cycle could partially mitigate the increase of atmospheric CO₂ concentration in the short-term. In the mid-term, thanks to a larger implementation of BECC and DAC, it could reduce absolute atmospheric CO₂ concentration. Some of the processes described in this article are already implemented at different scales. Integration would make them more efficient and sustainable, and help to implement them at a larger scale.

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